Nanostructured Design of Sulfur Cathode for High-Energy Lithium-Sulfur Batteries

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June 13, 2019

Project ID
bat230

Overview

Timeline

- Start: August 1, 2017
- End: October 31, 2020
- Percent complete: 60%

Budget

- Total project funding
  $900k from DOE
- Funding for FY18
  $300k
- Funding for FY19
  $300k

Barriers

Barriers of batteries
- High cost (A)
- Low energy density (C)
- Short battery life (E)

Targets: cost-effective and high-energy electrode materials and batteries

Partners

- Collaboration
  - BMR program PI's
  - SLAC: In-situ X-ray
  - Prof. Steven Chu, Stanford
  - Prof. Zhenan Bao, Stanford
  - PNNL scientists: Jun Liu, Jie Xiao

Project Objective and Relevance

Objective

- Develop lithium-sulfur batteries to power electric vehicles (HEV/PEV/EV) and decrease the high cost of batteries.

- Develop sulfur cathodes with high capacity and stability to generate high energy lithium-sulfur batteries with long cycle life.

- Design and fabricate novel nanostructured sulfur cathode with multifunctional coatings to overcome the materials challenges that lead to short battery life, including volume expansion, active material loss and low conductivity of sulfur cathode.

- Develop scalable low-cost methods for the synthesis of nanostructured sulfur cathode.

- Project contents are directly aimed at the listed barriers: high cost, low energy density and short battery life.

Milestones for FY18 and 19

Month/year	Milestones
1/2018	Elucidate different adsorption mechanisms and probe possible adsorption species (completed)
4/2018	Develop multi-functional sulfur cathode binder capable of controlling of the polysulfide shuttling and facilitating Li ion transport (completed)
7/2018	Demonstrate the flame-retardant property of binder to improve safety and propose flame-retardant mechanism (completed)
10/2018	Build *in situ* characterization platform to monitor nucleation/dissolution of sulfur/Li_2S_n (completed)
1/2019	Develop a non-invasive imaging method with sub-micron, sub-second resolution for Li-S battery in label-free, native organic liquid electrolyte (completed)
4/2019	Demonstrate the substrate-dependent electrochemical formation of super-cooled liquid sulfur and crystals, as well as rapid solidification of a super-cooled sulfur droplet (On track)

Approach/Strategy

Advanced nanostructured sulfur cathodes design and synthesis

1) Engineer empty space into sulfur cathode to solve the problem of electrode volume expansion.
2) Develop novel sulfur nanostructures with multi-functional coatings for the confinement of sulfur/lithium polysulfides to address the issues of active materials loss and low conductivity.
3) Develop/discover optimal nanostructured materials that can capture the polysulfide dissolved in the electrolyte.
4) Develop space efficiently packed nanostructured sulfur cathode to increase the volumetric energy density and rate capability.
5) Identify the interaction mechanism between sulfur species and different types of oxides/sulfides, and find the optimal material to improve the capacity and cycling of sulfur cathode.

Structure and property characterization

1) Ex-situ transmission electron microscopy
2) Ex-situ scanning electron microscopy
3) Inductively Coupled Plasma elemental analysis
4) In operando X-ray diffraction and transmission X-ray microscopy

Electrochemical testing

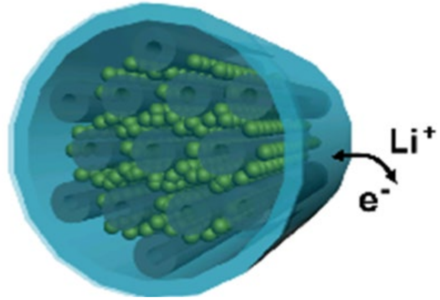
1) Coin cells and pouch cells
2) A set of electrochemical techniques

Previous Accomplishments on Sulfur Cathodes

Mesoporous carbon/S

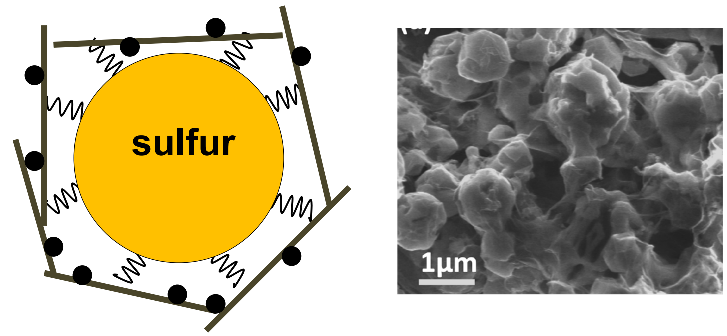
Nano Letters 10, 1486 (2010)

PEDOT/PSS-coated mesoporous carbon/S



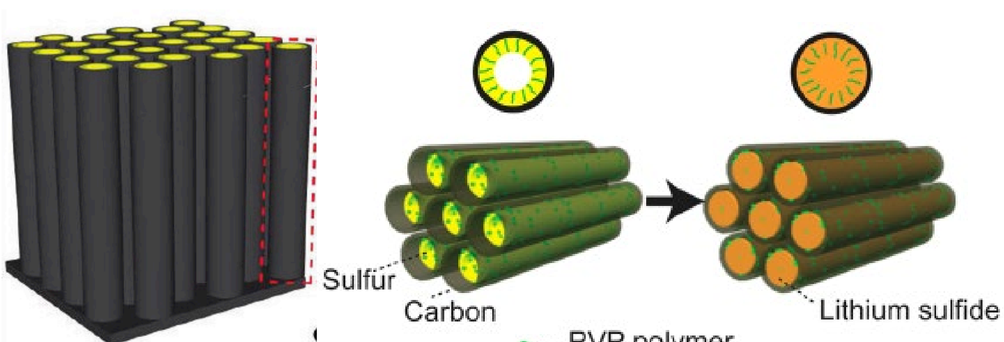
ACS Nano 5, 9187 (2011)

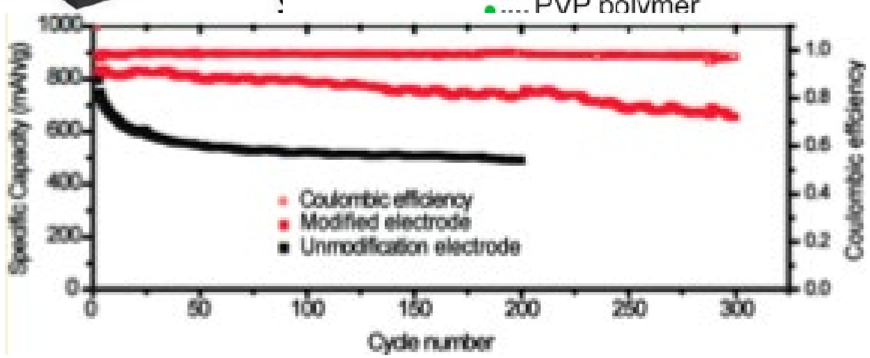
Graphene-coated S particles



Nano Letters 11, 2644 (2011)

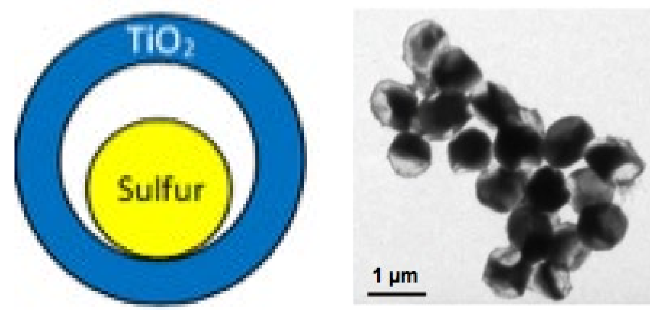
Hollow Carbon Fiber Encapsulated S

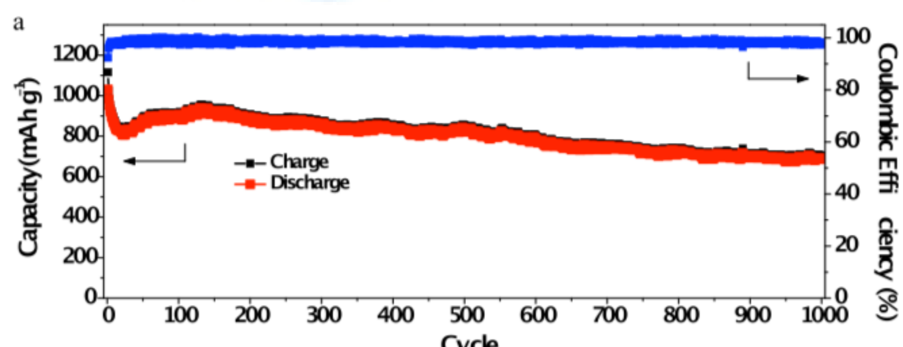




Nano Letters 11, 4462 (2011) *Nano Letters* 13, 1265 (2013)

Yolk-Shell S-TiO_2 Nanoparticles

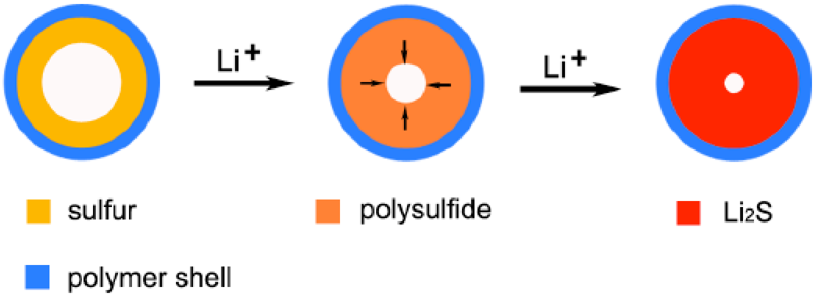


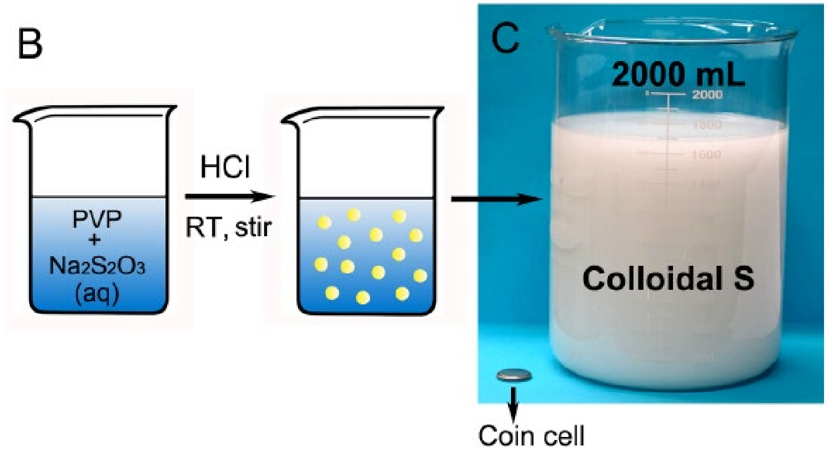


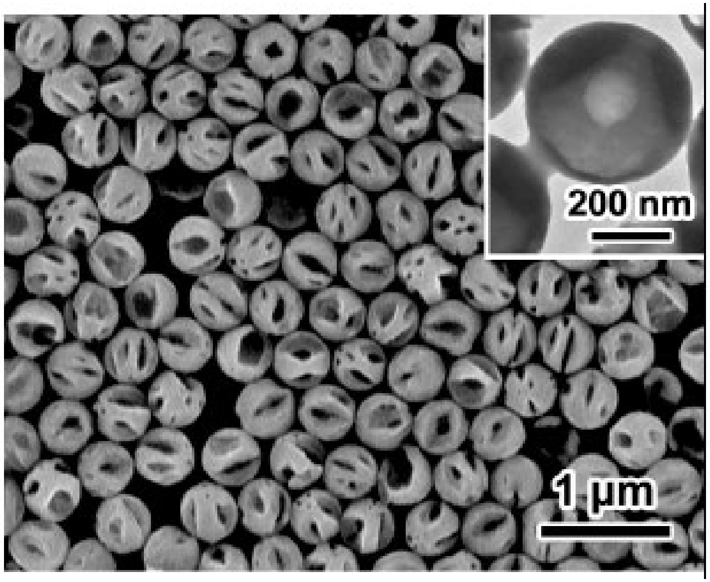
Nature Communication 4: 1331 (2013)

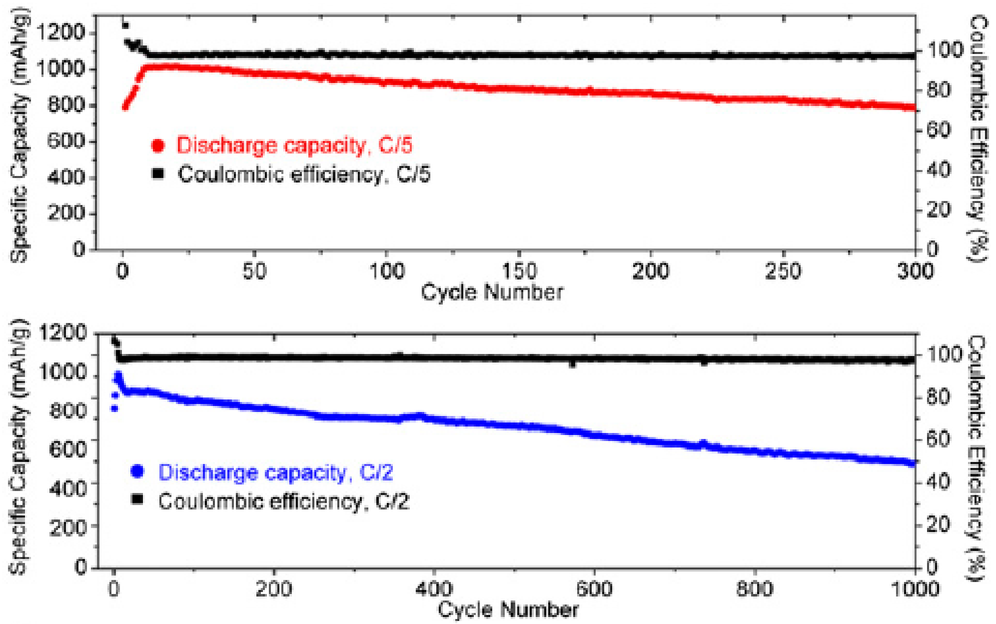
Accomplishment

Hollow S-Amphiphilic Polymer Nanoparticles









Cui group, *PNAS 110*, 7148 (2013)

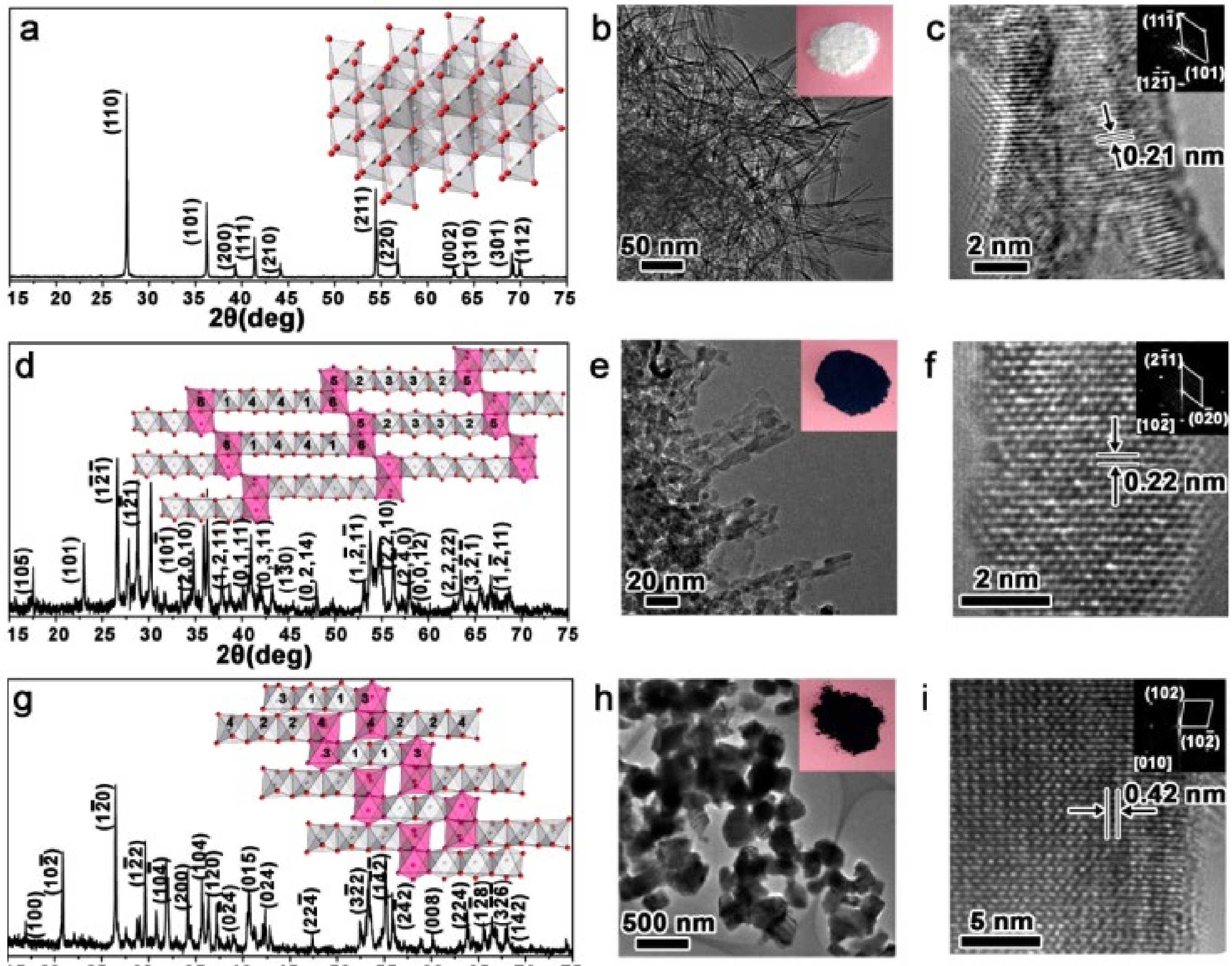
Accomplishment

Magnéli-Phase Ti_nO_{2n-1} Nanomaterials for S Cathodes

TiO_2

Ti_6O_{11}

Ti_4O_7

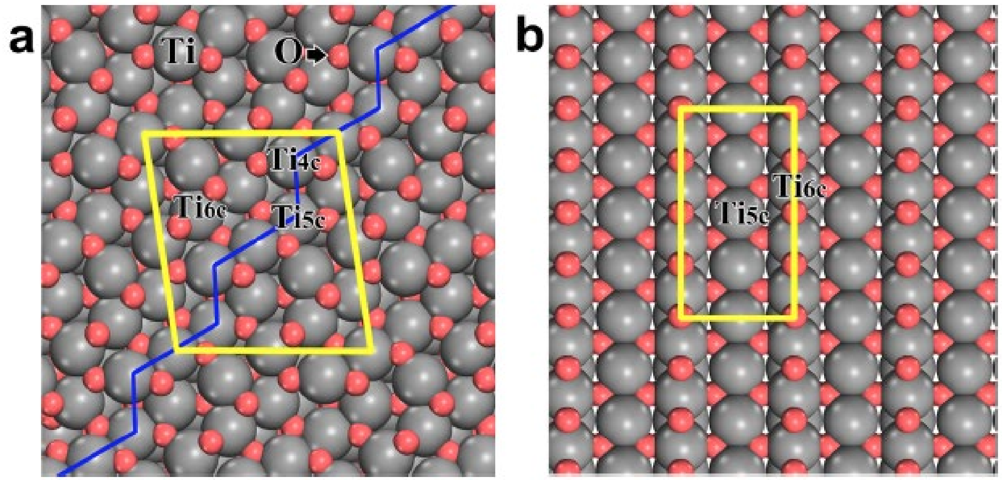


Cui group, *Nano Letters* 14, 5288 (2014)

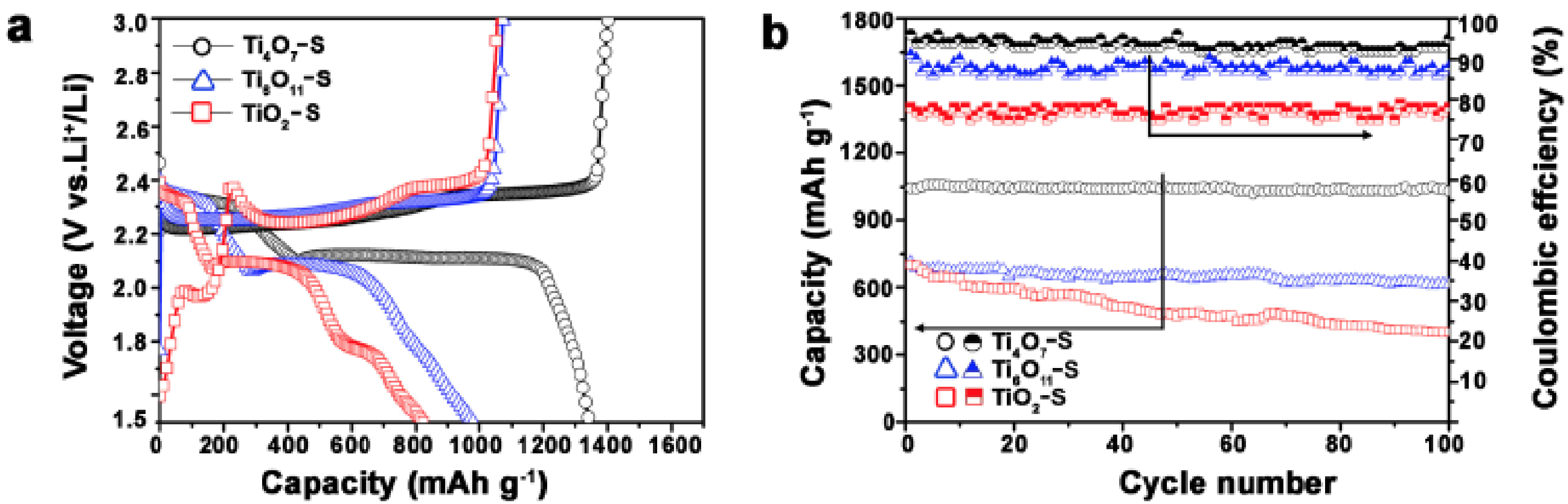
Accomplishment

Strong sulfur binding with conductive magnéli-phase Ti_4O_7 nanoparticles: Magnéli-Phase has high concentration of O vacancies

Ti_4O_7



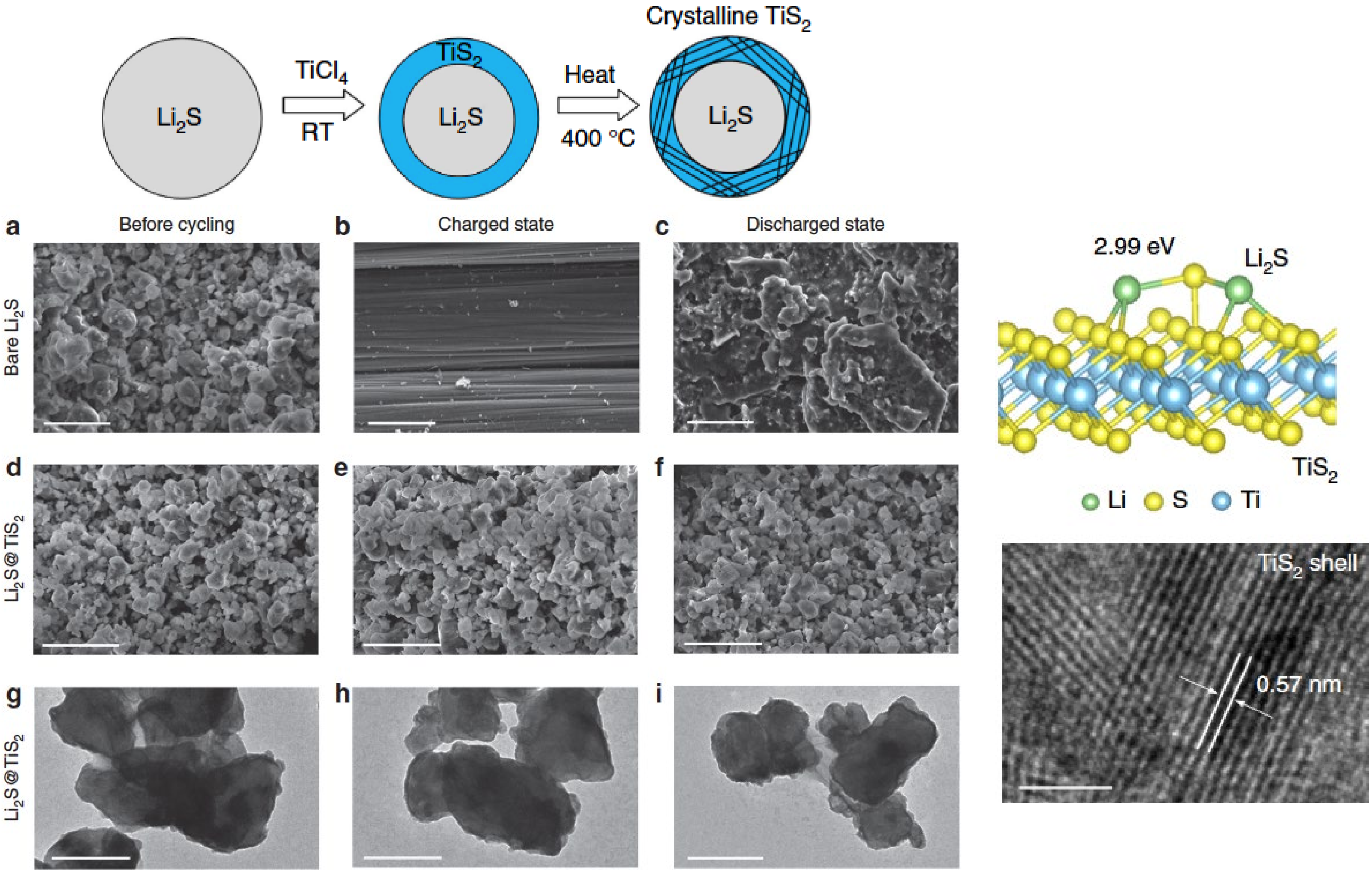
TiO_2



Cui group, *Nano Letters* 14, 5288 (2014)

Accomplishment

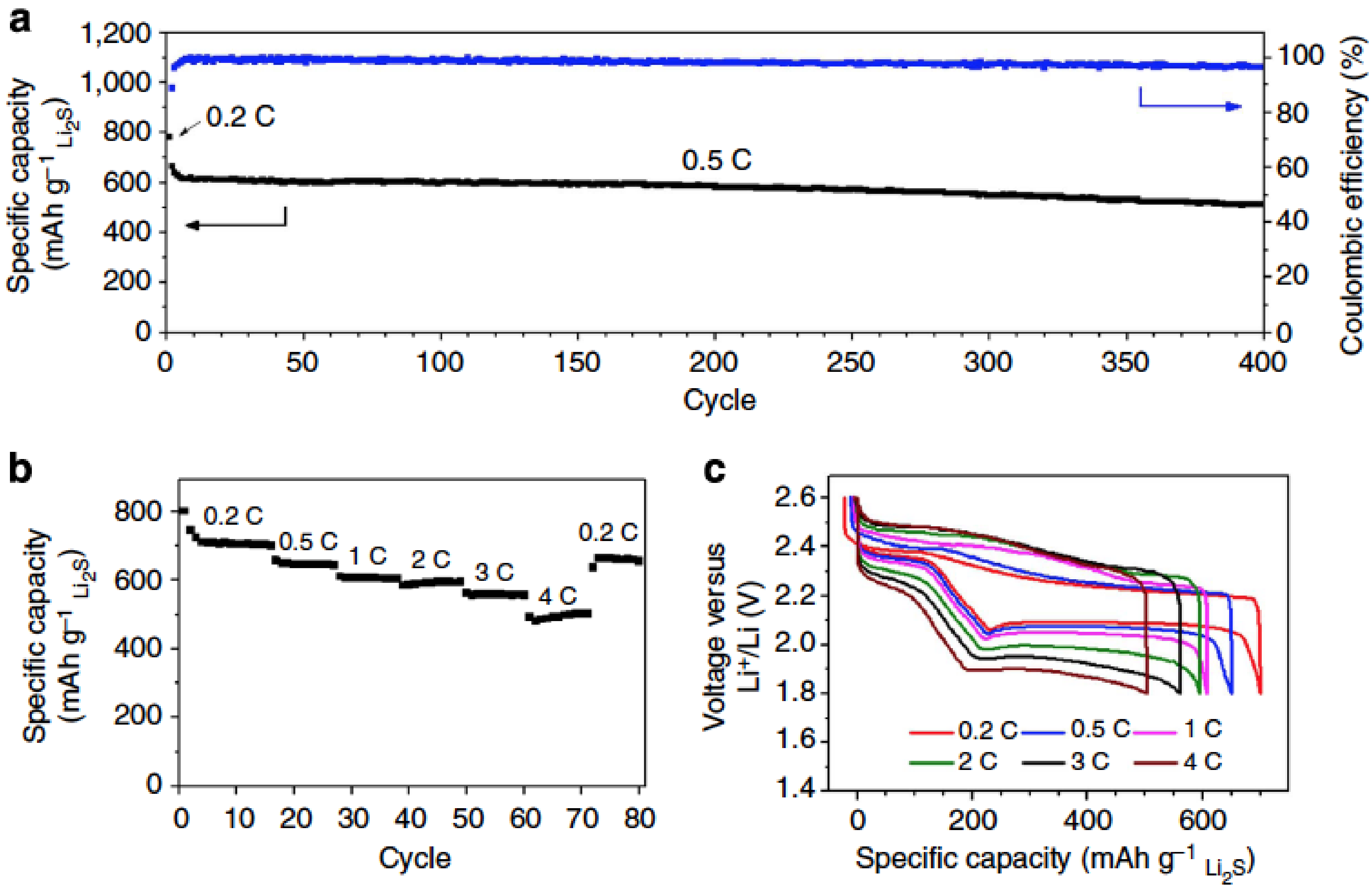
2D layered MS_2 for Effective Encapsulation of Li_2S Cathodes



Cui group, *Nature Communications* 5:5017 (2014)

Accomplishment

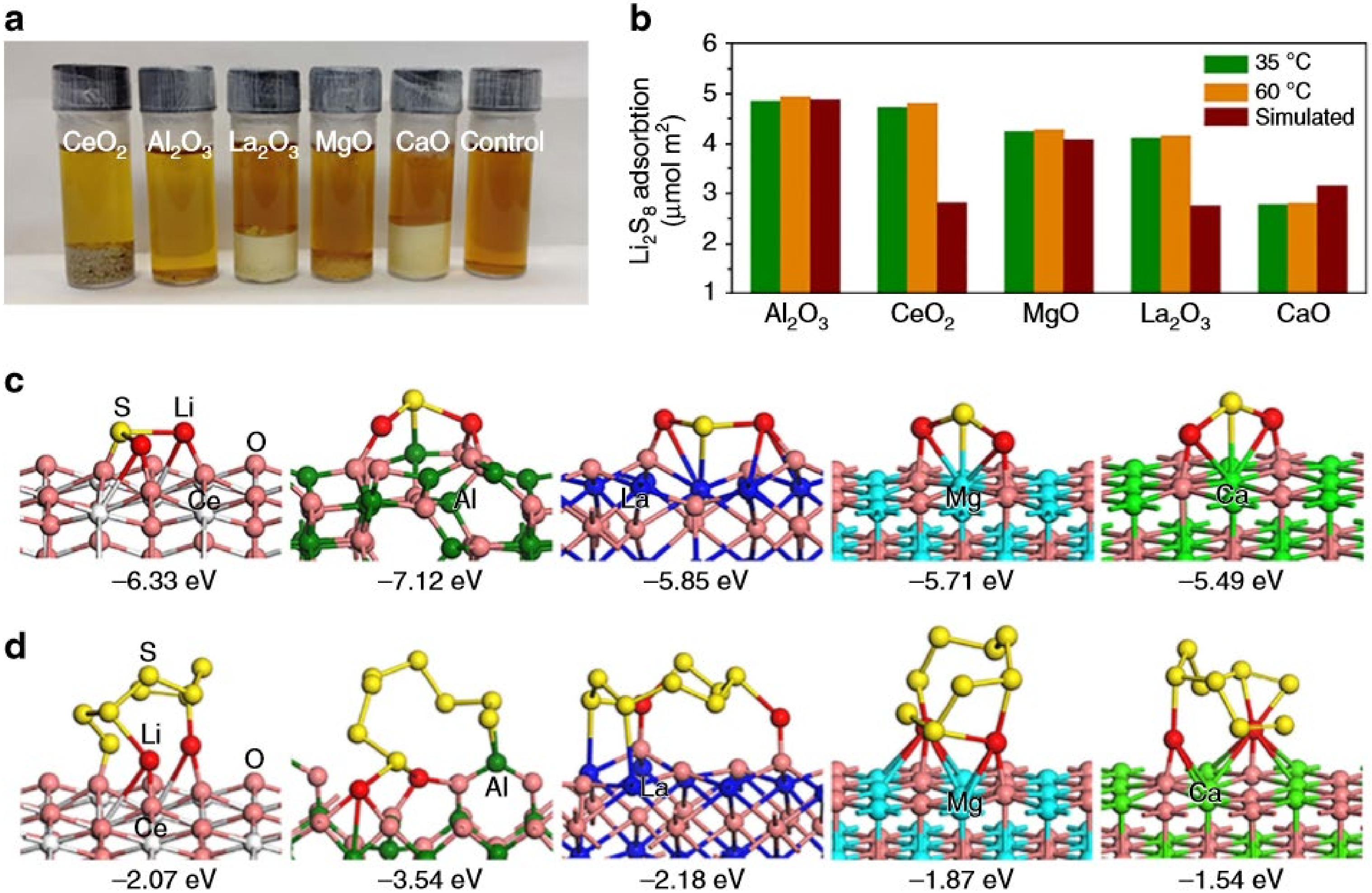
TiS_2-Li_2S Cathodes: battery performance



Cui group, *Nature Communications* 5:5017 (2014)

Accomplishment

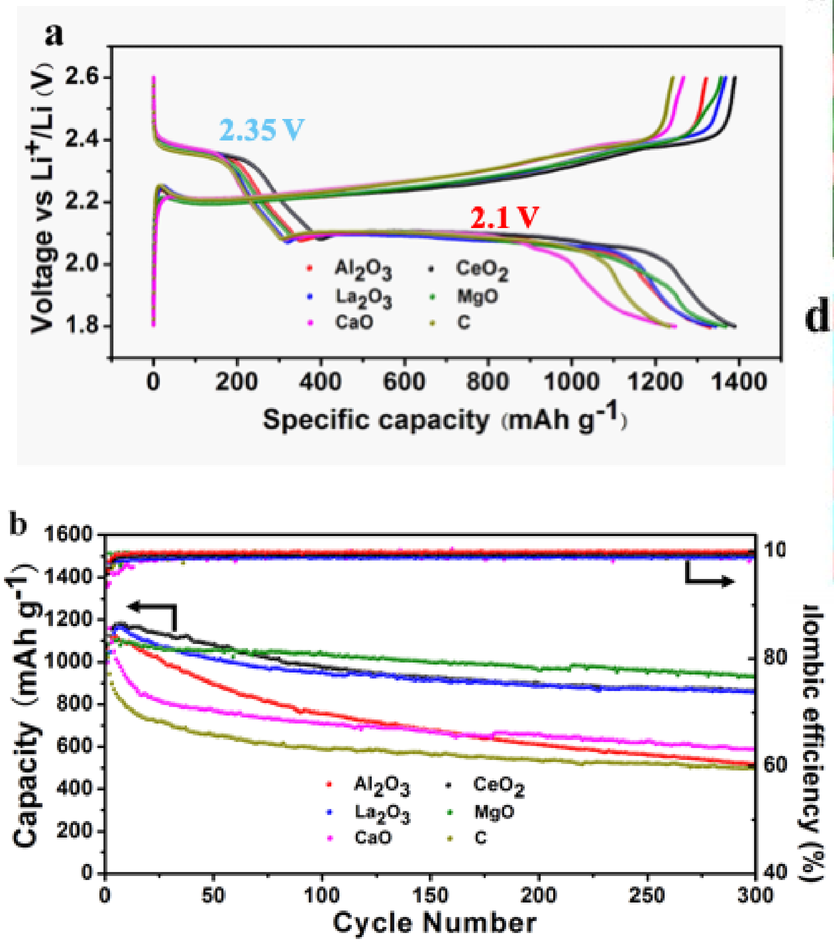
Polysulfide capture on the surface of metal oxides is monolayered chemisorption confirmed by combined experiment-DFT computations

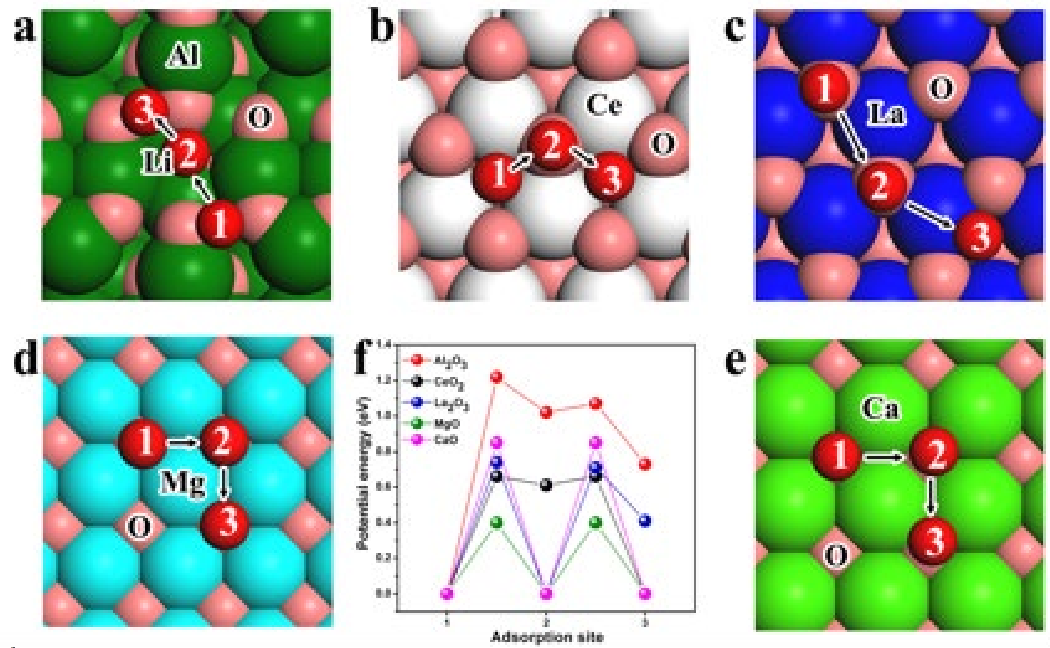


Cui group, Nature Communications, 7, 11203 (2016)

Accomplishment

Oxide selection criterion: balance optimization between sulphides adsorption and diffusion on the metal oxides surface



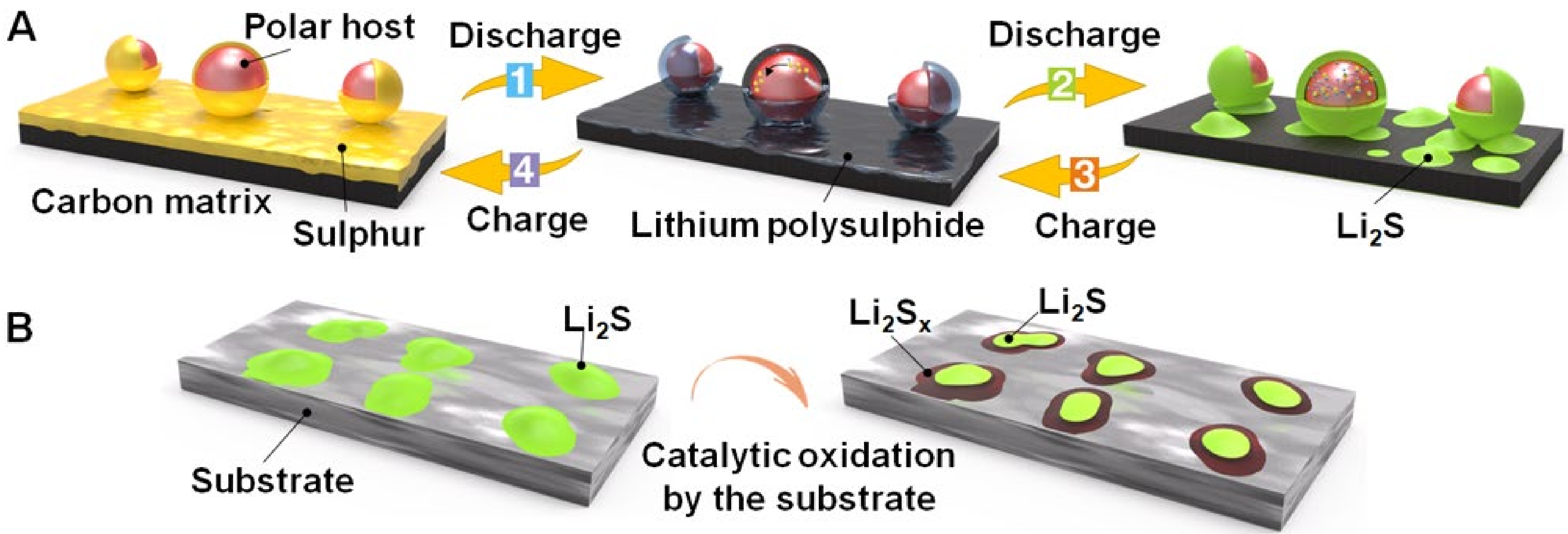


➢ Lithium sulphide species can strongly adsorb, however, difficult to diffuse on Al_2O_3
➢MgO with suitable adsorption energies of lithium sulphur species and small diffusion barriers of Li
➢CeO_2(111) and La_2O_3(001) surfaces with similar diffusion barrier of 0.66 eV have the similar cycling performance.

Cui group, Nature Communications, 7, 11203 (2016)

Accomplishment

Sulphur adsorption and conversion process



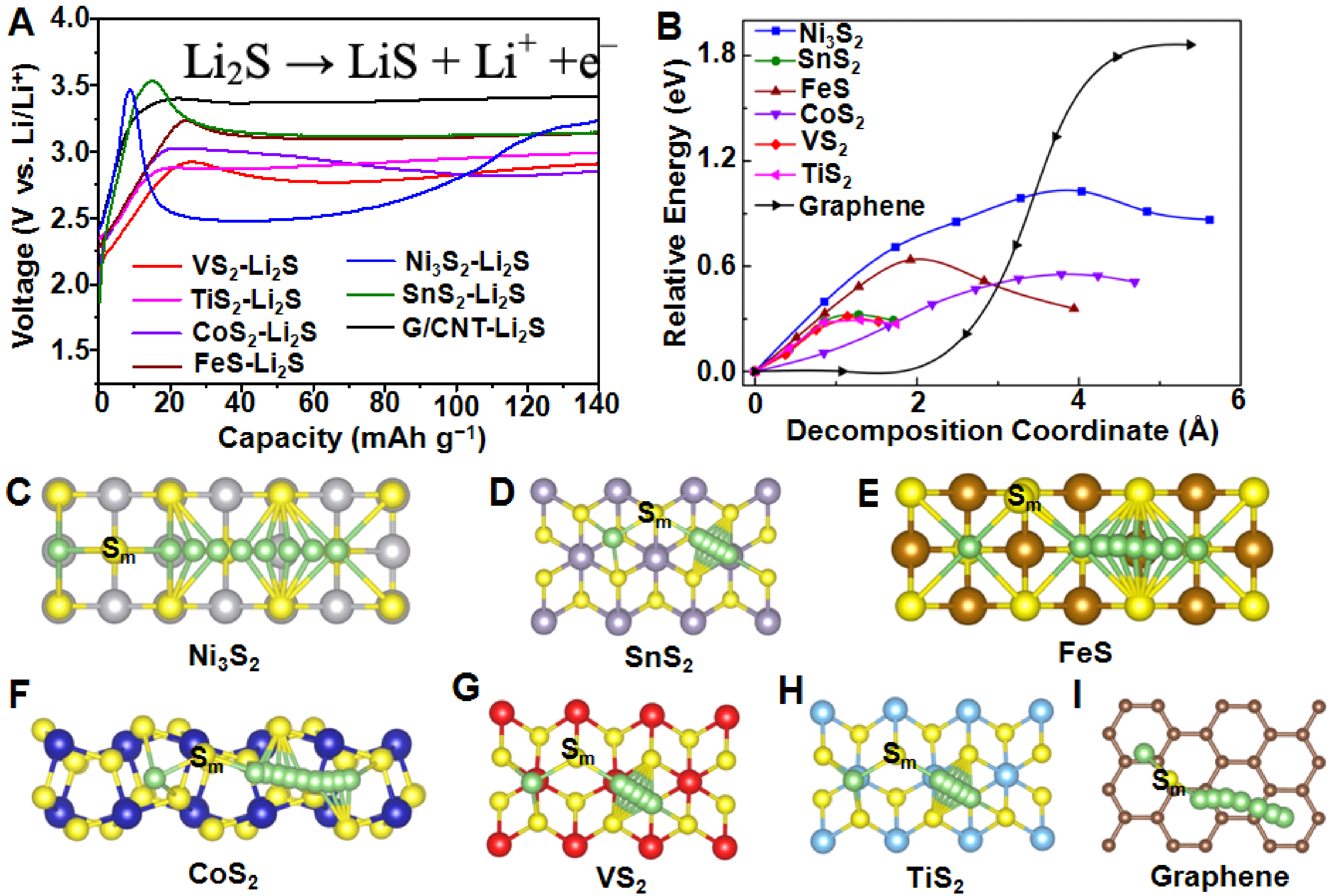
Both electrochemical and chemical reaction happen during battery cycling

Disproportionation reaction Li_2S_4 => Li_2S + Li_2S_8

Cui group, PNAS, 114, 840 (2017)

Accomplishment

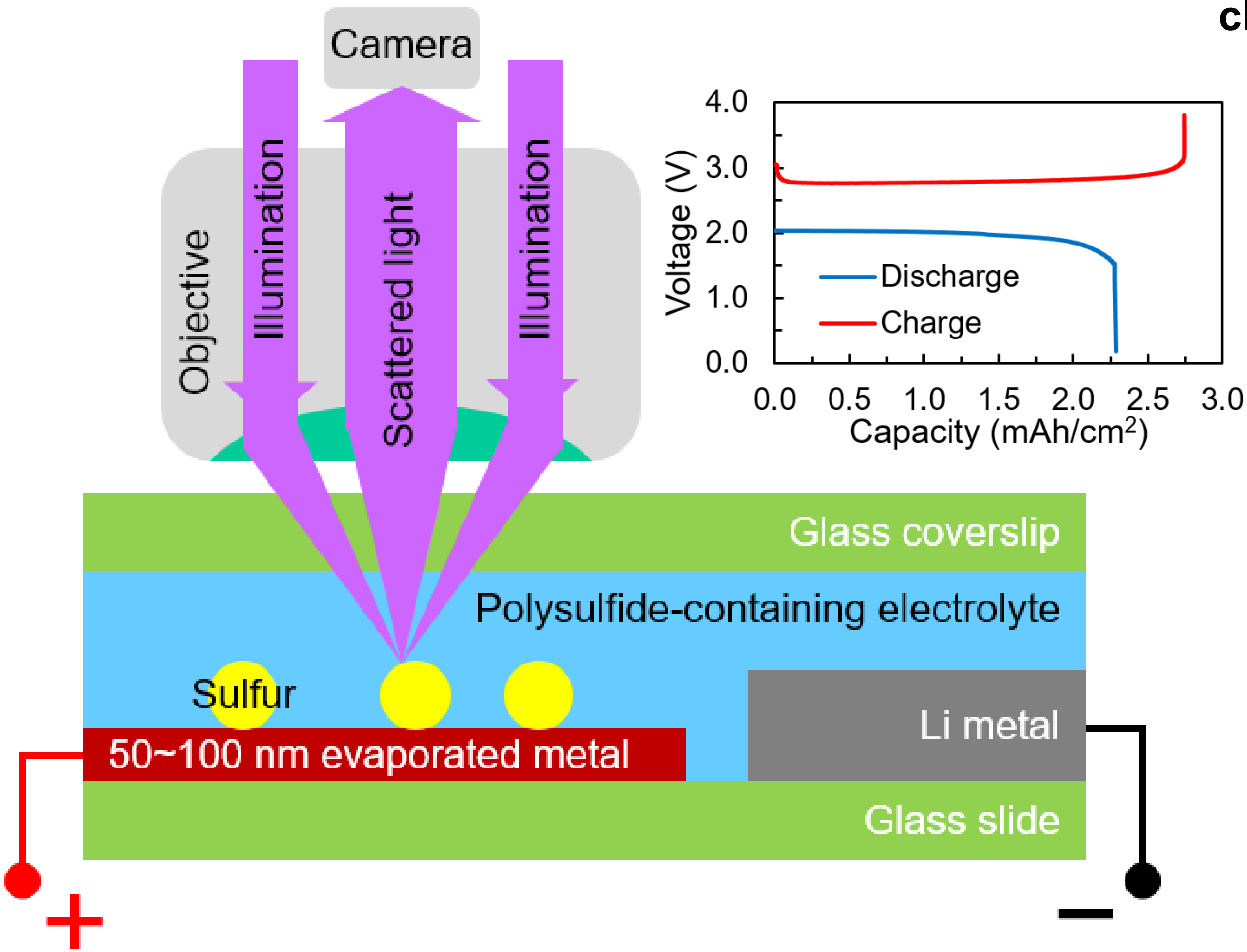
Catalytic effects of substrate: decomposing barriers for Li_2S



Cui group, PNAS, 114, 840 (2017)

Accomplishment

Transparent Li-S cell for light microscopy



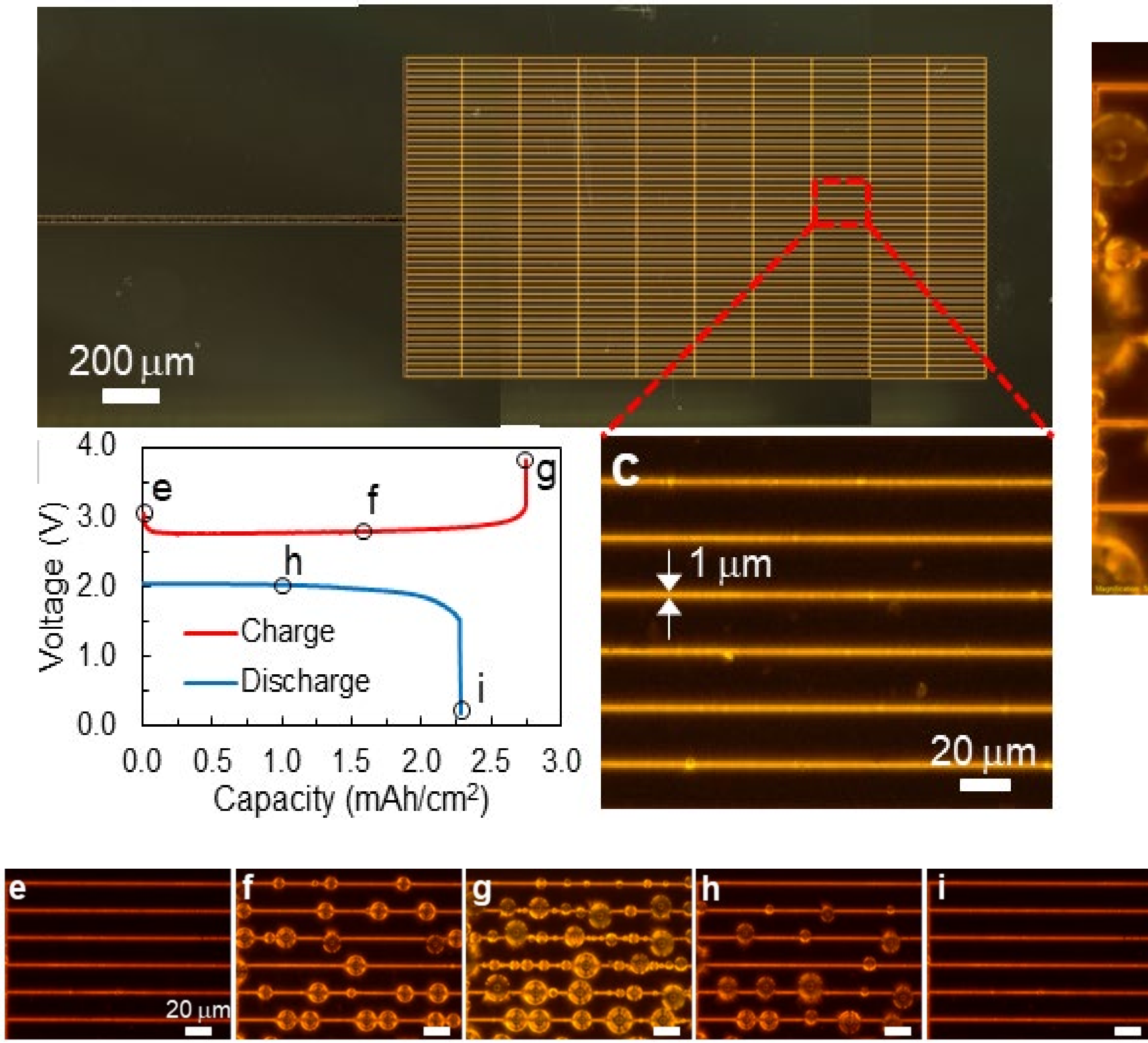
Probing sulfur electrochemistry challenges:

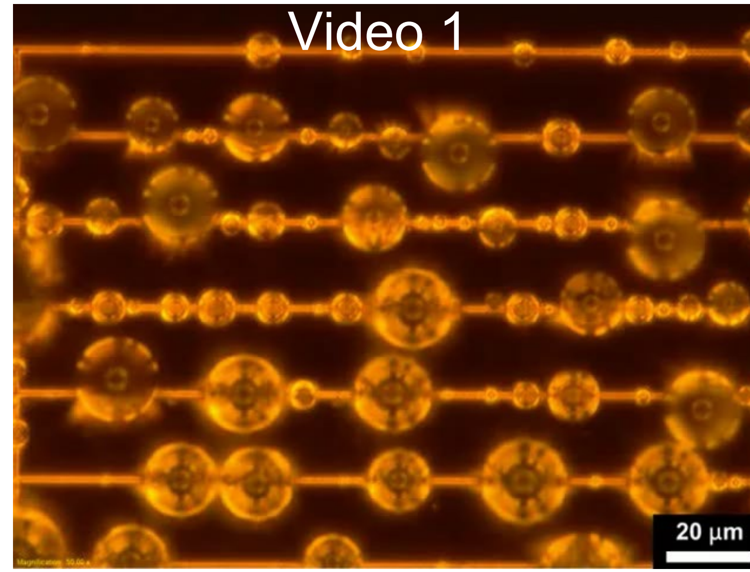
- Sulfur species are sensitive to vacuum, electron beam irradiation and X-ray irradiation, which limits the diagnostic tools;
- Sulfur has multiple reaction pathways, which could be easily disturbed by added indicators or labels;
- The materials easily change upon removing from native electrolyte, hence requiring *in operando* study.

Cui group, PNAS, 116, 765 (2019)

Accomplishment

Transparent Li-S cell for light microscopy



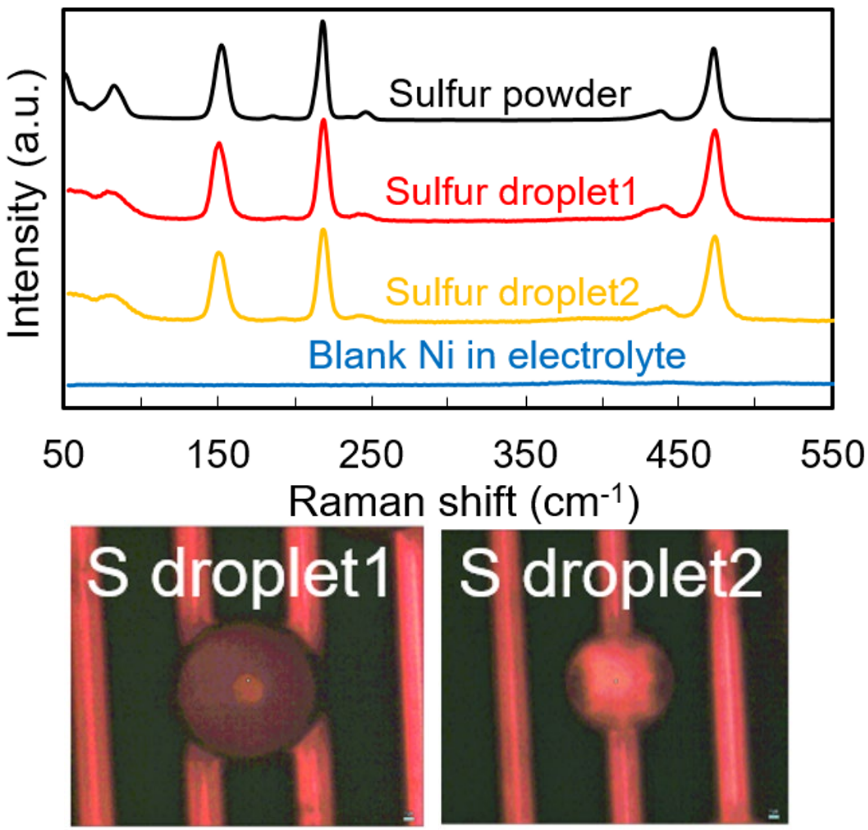


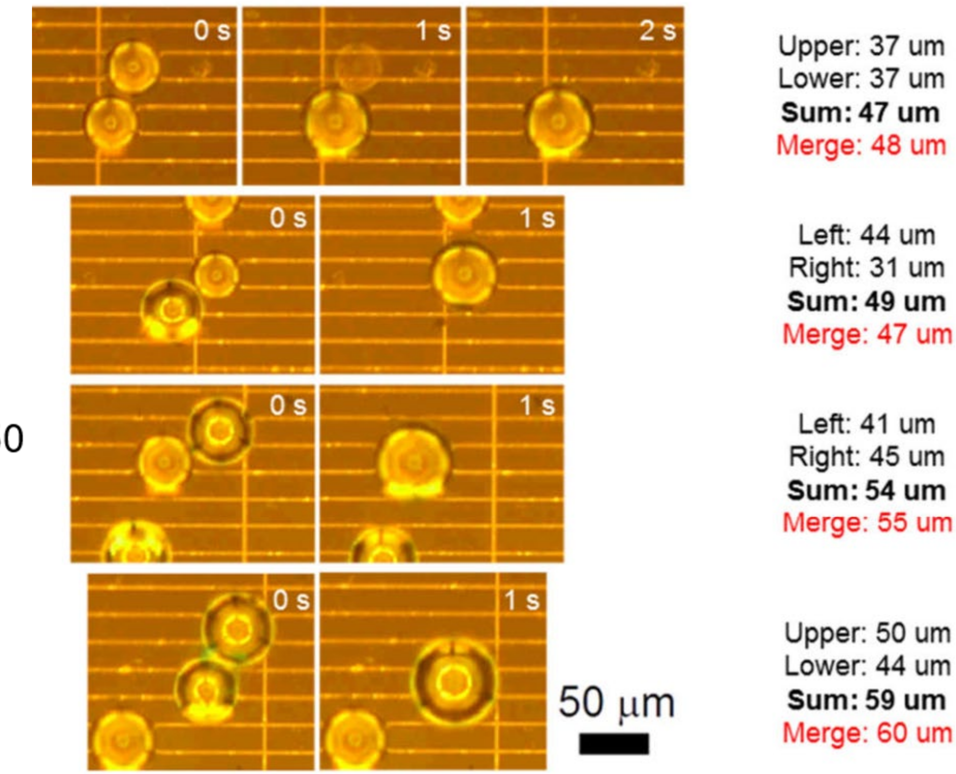
Cyclo-S_8
Melting point: 115.2^{o}C

Cui group, PNAS, 116, 765 (2019)

Accomplishment

Raman spectra of these droplets

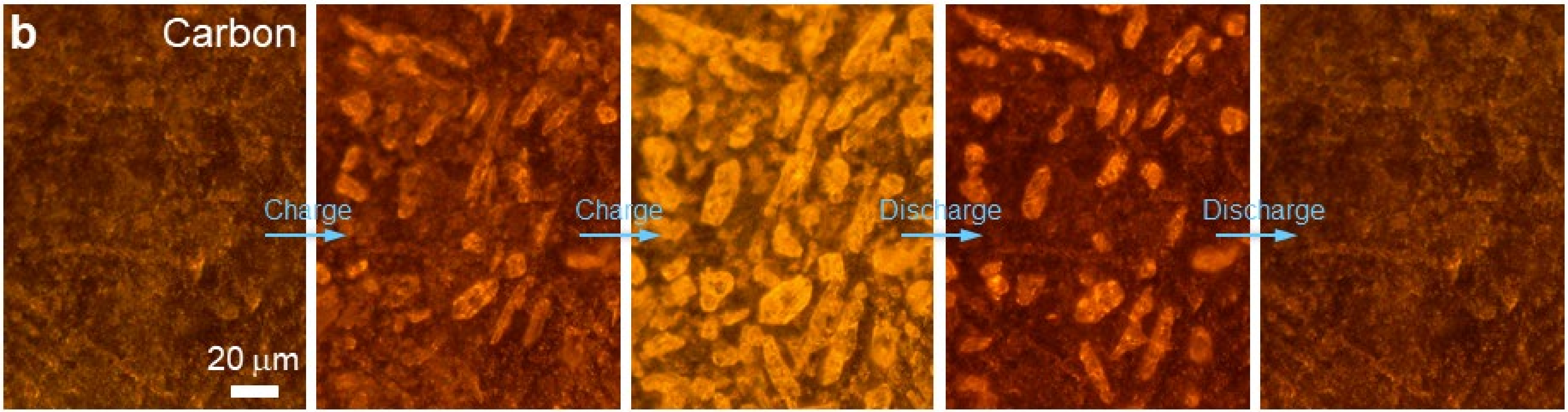


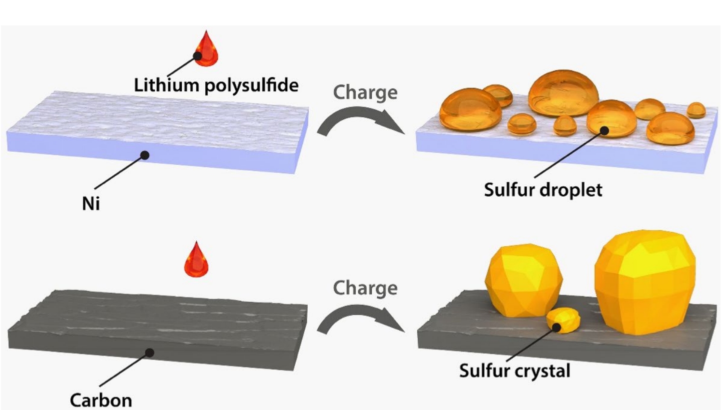


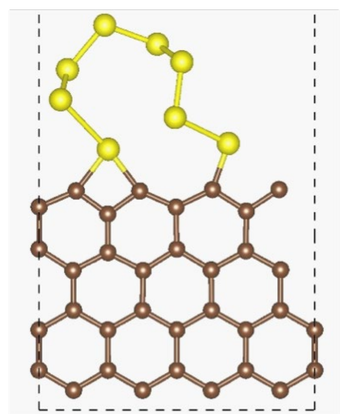
Cui group, PNAS, 116, 765 (2019)

Accomplishment

Sulfur crystal formation on carbon

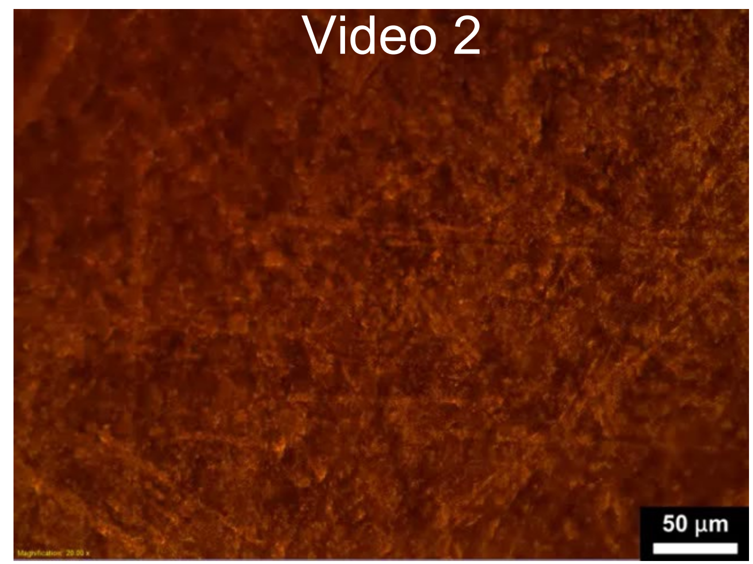






Graphene Zigzag edge

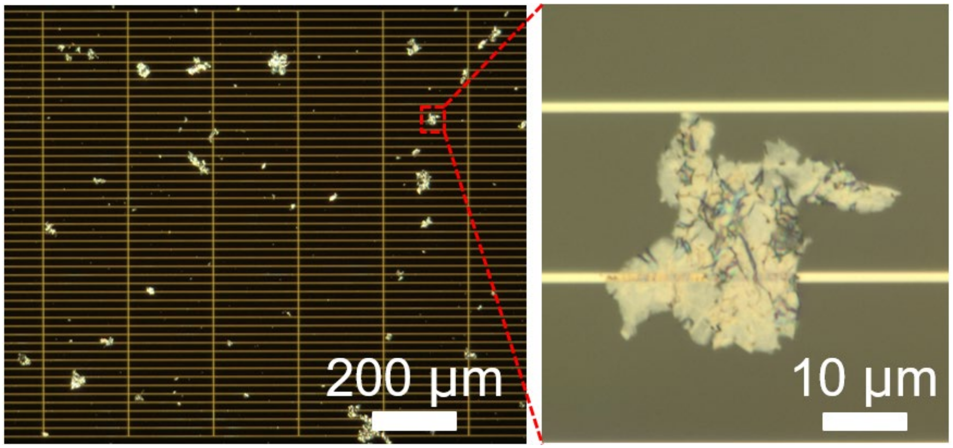
E_{ad} = -3.21 eV

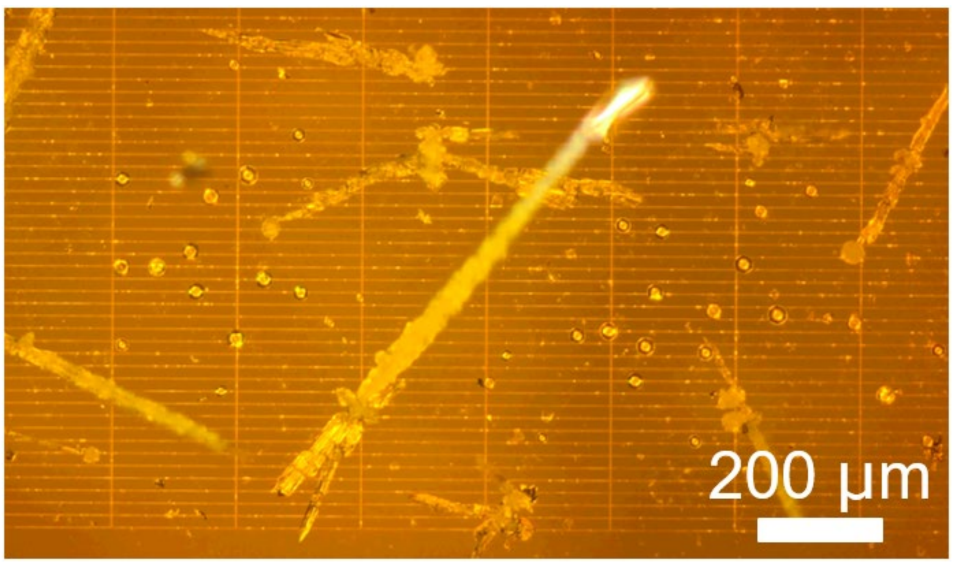


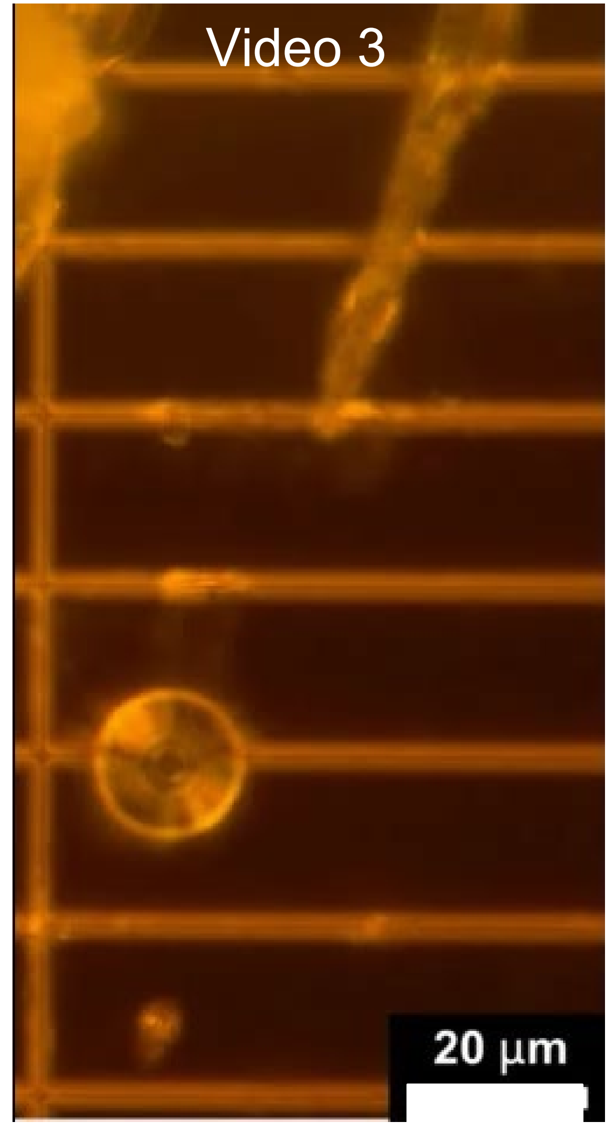
Cui group, PNAS, 116, 765 (2019)

Accomplishment

Rapid solidification of super-cooled liquid sulfur







Cui group, PNAS, 116, 765 (2019)

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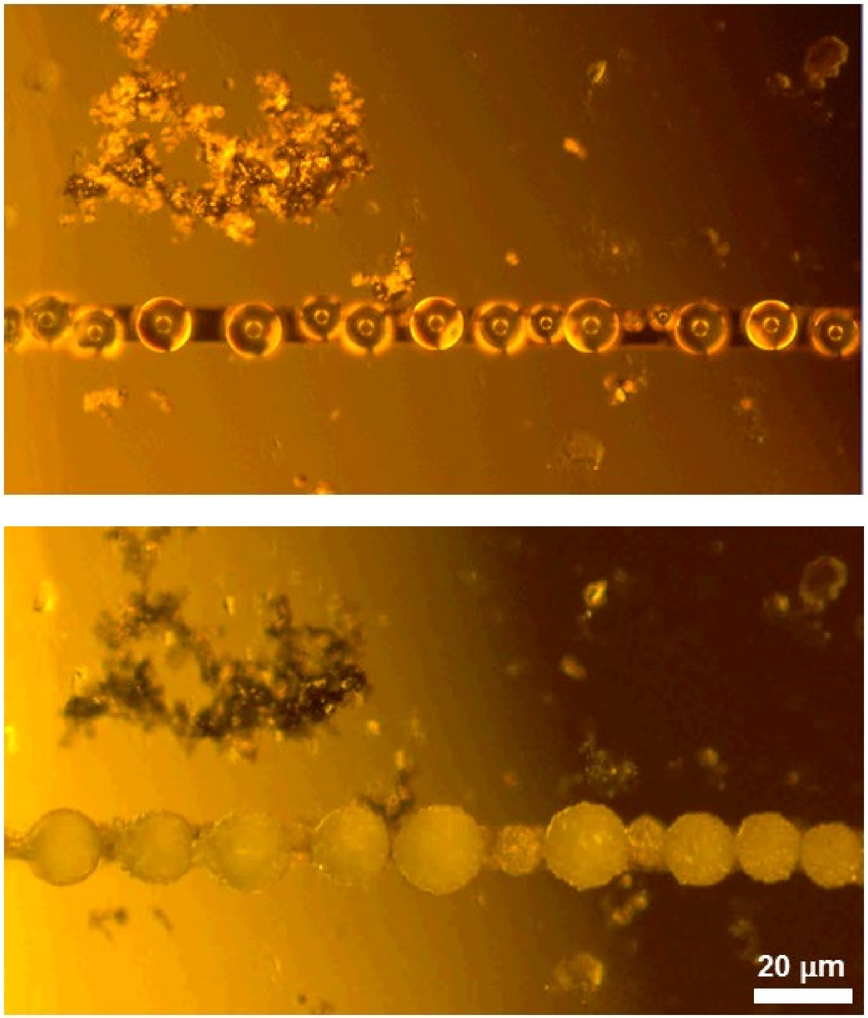
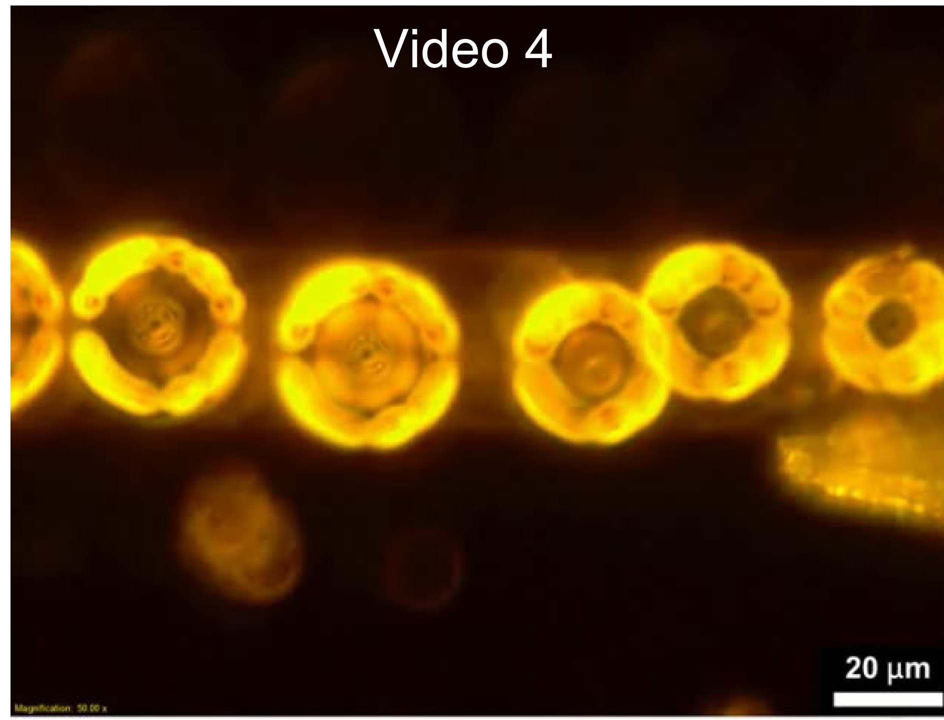
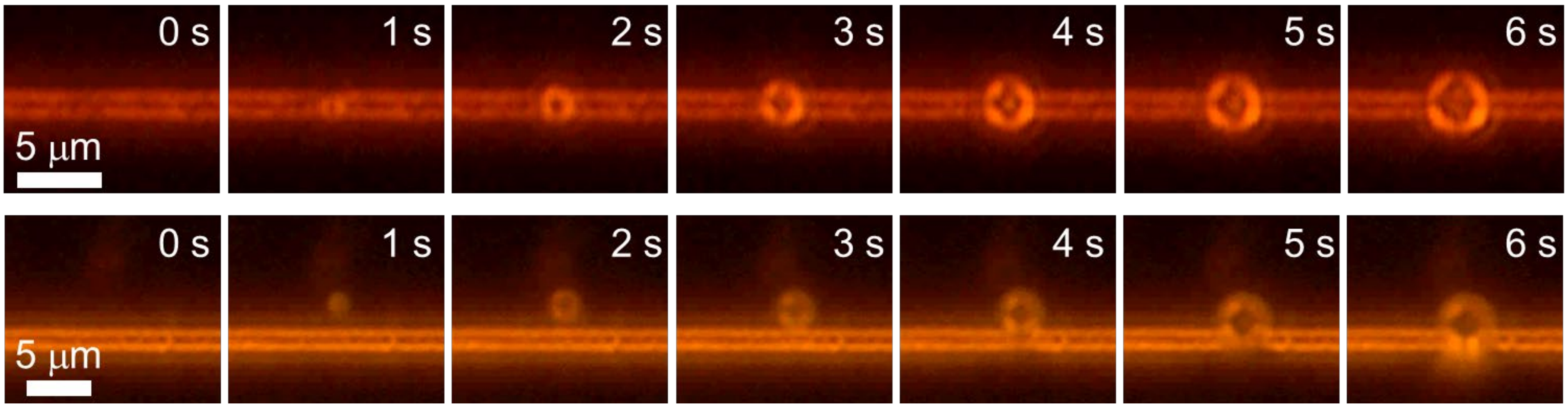


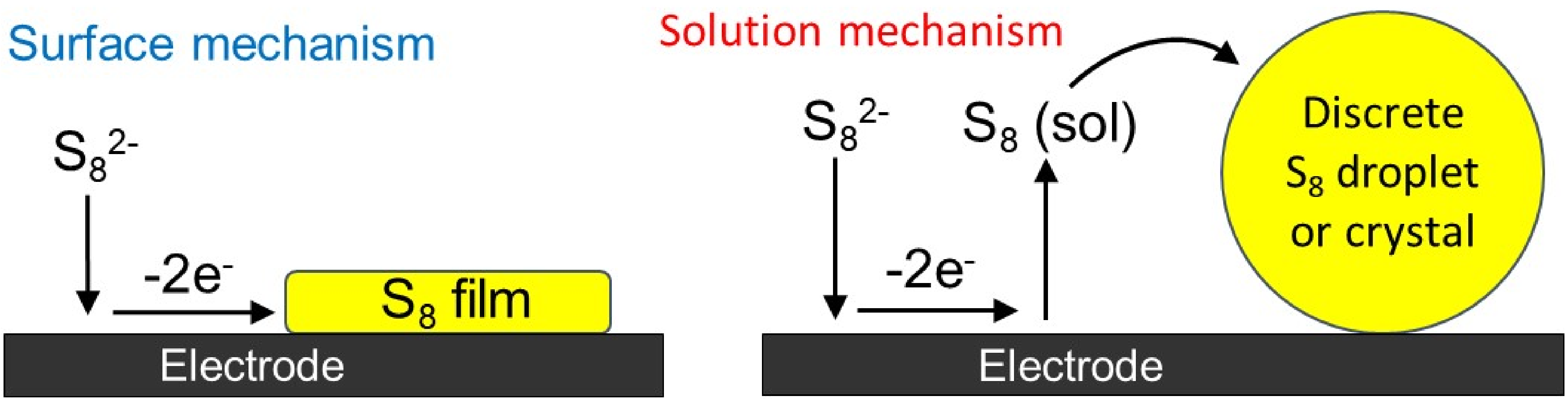


Cui group, PNAS, 116, 765 (2019)

Accomplishment

Surface or solution mechanism in Li-S batteries?





Cui group, PNAS, 116, 765 (2019)

Responses to Previous Year Reviewers' Comments

Overall review comment: The project is innovative and productive and has an excellent value.

Review suggestions to improve:
Suggestion: Reviewer suggest to have more collaboration with domestic institutions
Response: We have established multiple collaboration inside Stanford and with PNNL national lab.

Suggestion: Reviewers suggest to control the volume of electrolyte.
Response: We have recently been conducting research under the lean electrolyte condition.

Suggestion: Reviewers suggest to work on Li metal anode problem in the Li-S batteries.
Response: We have been conducting research extactly along this direction. We have a program working on Li metal anodes and are now doing testing inside Li-S cell.

Collaboration and Coordination

Stanford University:
- Prof. Steven Chu
- Prof. Zhenan Bao

SLAC:
In-situ X-ray, Prof. Mike Toney

PNNL:
- Dr. Jun Liu
- Dr. Jie Xiao

Remaining Challenges and Barriers

- It is difficult to maintain high capacity and excellent cycling stability of lithium-sulfur batteries while increasing the mass loading of active sulfur in the cathode.

- It is challenging to improve the rate capability (performance of battery at high current densities) of lithium-sulfur batteries.

- It is difficult to fully prevent all the active sulfur species from diffusing into the electrolyte.

- The volumetric energy density of lithium-sulfur batteries needs to be further increased.

- The lithium dendrites grown on the lithium metal surface is a concern for the safety of lithium-sulfur batteries that use lithium metal as anodes.

Summary

- **Objective and Relevance:** The goal of this project is to develop stable and high capacity sulfur cathodes from the perspective of nanomaterials design to enable high energy lithium-sulfur batteries to power electric vehicles, highly relevant to the VT Program goal.
- **Approach/Strategy:** This project combines advanced nanomaterials synthesis, characterization, battery assembly and testing, and guided by theoretical calculations, which have been demonstrated to be highly effective.
- **Technical Accomplishments and Progress:** This project has produced many significant results, meeting milestones. They include identifying the key issues in lithium-sulfur batteries, using rational materials design, synthesizing and testing, and developing scalable and low-cost methods. The results have been published in top peer-reviewed scientific journals. The PI has received numerous invitations to speak in national and international conferences.
- **Collaborations and Coordination:** The PI has established a number of highly effective collaborations.
- **Proposed Future Work:** Rational and exciting future has been planned.

Proposed Future Work

- To develop space efficiently packed nanostructured sulfur cathode to increase the volumetric energy density.
- To improve the interparticle contact and conductivity of sulfur nanostructures to increase the kinetics and thus improve the rate capability.
- To test sulfur cathodes with high areal mass loading up to 5 mg/cm^2 at high current densities.
- To develop approaches to prevent the lithium dendrites growth on lithium metal anodes in lithium-sulfur batteries
- To combine lithium sulfide cathodes with non-lithium anodes, such as silicon, to assemble full batteries to eliminate the safety concern of using lithium metal.
- To develop high performance lithium-sulfur batteries under lean electrolyte.